Kinetics and Mechanism of Oxidation of Hydroquinone by Tetrabutylammonium Tribromide Ion in Aqueous Acetic Acid

S.N. Zende · V.A. Kalantre · G.S. Gokavi

Abstract The oxidation of hydroquinone by environmentally benign tetrabutyl ammonium tribromide (TBATB) was carried out in 50% V/V aqueous acetic acid medium under pseudo-first-order conditions, keeping a large excess of hydroquinone over the oxidant. The main reactive species of oxidant and substrate were found to be the Br_3^- ion and hydroquinone, respectively. The reaction proceeds with prior complex formation between the reactants followed by its slow decomposition to generate semiquinone and bromine radicals. The complex formation was kinetically verified by its Michaelis–Menten plot. The solvent effect was verified by using Grunwald–Winstein equation which is consistent with an S_N2 mechanism. The formation constants for the complex and rate constant for the slow decomposition step were determined by studying the reaction at five different temperatures. The values of formation constant of the complex and the rate constant for its decomposition were determined at these temperatures. The activation parameters with respect to the slow step of the reaction have also been determined.

Keywords Hydroquinone · Mechanism · Oxidation · Tetrabutylammonium tribromide

1 Introduction

The oxidative conversion of hydroquinone to *p*-benzoquinone is a two-electron process which has been carried out by variety of oxidants, including: $[Ni^{III}(cyclam)]^{3+}$ [1], $[Ni^{IV}(oxime)]^{2+}$ [2], $[Mn^{III}\text{-}(EDTA)]$ [3], $[Rh_2(O_2CCH_3)_4(OH_2)_2]^+$ [4], iron(II) porphyrins [5], $[Cu^{II}(dmp)_2]^{2+}$ [6], $[Ru^{III}(CN)_6]^{3-}$ [7], trans-$[Ru^{IV}(tmc)(O)]^{2+}$ [8], $[Ru^{IV}(bpy)_2(py)(O)]^{2+}$ [9], VO^{2+} [10], $Cu^{2+}(aq)$ [11] and $[Fe_2(\mu\text{-}O)(phen)_4(OH_2)_2]^{4+}$ [12].

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The oxidation of hydroquinone usually proceeds through an initial, rate determining, one electron-transfer step, irrespective of whether the oxidant is a one or two-electron oxidant, generating the semiquinone radical. The second, fast, step of the reaction involves either further oxidation of the semiquinone radical by the oxidant or disproportionation to give the final product benzoquinone. Depending upon the reactive species of the hydroquinone in aqueous acidic solutions, various possible of mechanisms involving proton and electron transfer for the oxidation of hydroquinone by trans-$[Ru^{IV}(tmc)(O)]^{2+}$ have been verified [8]. The mechanism involving slow concerted proton and electron transfer has been found to be thermodynamically favorable. Such a proton transfer coupled electron transfer mechanism is probable if the oxidant and its reduced state undergo protonation. In order to understand the mechanism of oxidation of hydroquinone by an oxidant which is a strong electrolyte, both in its oxidized or reduced form, the present study was undertaken. The oxidant in the present study, tetrabutylammonium bromide, and its product bromide are both strong electrolytes in aqueous acidic solutions thus providing an opportunity to study the nature of the electron-transfer mechanism of the oxidation of hydroquinone. Tetrabutylammonium tribromide is comparatively less hazardous, stable, solid and environmentally benign [13] reagent than molecular bromine; it can be prepared by oxidizing bromide to tribromide and then precipitating with a quaternary ammonium cation [13]. Such tetraalkylammonium polyhalides have been used in various organic transformations [14] and for oxidation of organic [15] and inorganic [16] substrates. Oxidations by TBATB are generally studied in 50% acetic acid as the reagent is stable in such a medium. The main reactive species of the reagent in aqueous solutions is Br_3^- formed from TBATB dissociation. Further dissociation of Br_3^- into bromide ion [17] and molecular bromine also occurs, which can be suppressed by adding an excess of bromide ions to the solutions. Oxidations [17, 18] by TBATB generally follow a mechanism involving prior complex formation with the substrate followed by its decomposition. The decomposition of the complex formed may proceed either by one-electron or by direct two electron transfer between the reactants. In continuation of our work [15, 16] in the use of tetrabutylammonium tribromide (TBATB) for oxidation of inorganic and organic substrates, the present work of oxidation of hydroquinone by TBATB was undertaken.

2 Experimental

2.1 Materials and Methods

All the chemicals used were of reagent grade and doubly distilled water was used throughout. The oxidant TBATB was synthesized by the reported procedure [13] and stock solutions was obtained by dissolving known quantity of TBATB in 50% acetic acid. The standardization of TBATB was carried out both iodometrically and spectrophotometrically. Hydroquinone (SD fine) was used. The solution of hydroquinone was prepared by dissolving it in distilled water. The acetic acid (Thomas Baker) and potassium bromide (SD fine) were used as received. The reaction mixture, in all kinetic runs, contained a constant concentration of potassium bromide of 0.01 mol·dm^{-3} in order to prevent the dissociation [17] of the tetrabutylammonium tribromide ion. Kinetic runs were carried out under pseudo-first-order conditions keeping a large excess of hydroquinone. The solutions containing the reactants and all other constituents were thermally equilibrated at 25 ± 0.1 °C separately, mixed and the reaction mixture was analyzed for unreacted TBATB at 394 nm using an Elico-SL-177 Spectrophotometer ($\varepsilon = 107 \pm 2$ dm^3·mol^{-1}·cm^{-1}). The values of the rate constants were reproducible to within ±5%.

Table 1 Effect of tetrabutylammonium tribromide (TBATB) concentration on k_{obs} in 50% V/V acetic acid at 25 °C. $10^2[H_2Q] = 1.0 \; mol \cdot dm^{-3}$, $10^2[KBr] = 1.0 \; mol \cdot dm^{-3}$

$10^3[TBATB] / mol \cdot dm^{-3}$	0.5	1.0	2.0	3.0	4.0	5.0
$10^3 k_{obs}/s^{-1}$	1.1	1.1	1.1	1.1	1.0	1.1

2.2 Product Analysis

The product analysis was carried under kinetic conditions. In a typical experiment, the hydroquinone (1.101 g, 0.1 mol) and TBATB (0.482 g, 0.01 mol) were taken in 100 cm³ acetic acid-water (1:1, V/V) and the reaction mixture was allowed to stand for 24 hours to ensure completion of the reaction. Then the reaction mixture was extracted with ether, and the acetic acid in the ether layer was neutralized using saturated sodium bicarbonate (NaHCO₃) and washed with distilled water. Then the ether layer was separated and evaporated to obtain *p*-benzoquinone as the product. The product was purified, weighed and confirmed by its melting point (0.864 g, 80%, m.p. 114 °C, lit. m.p. = 115 °C [19]). The FTIR spectral analysis of the product and substrate were carried out by using a Perkin Elmer Spectrum 100 instrument. The product showed peaks at 1633, 1516 and 3212 cm⁻¹ corresponding to $C = O$, $C = C$ and aromatic C–H stretches, while that of the hydroquinone shows peaks at 3400, 3212 and 1425 cm⁻¹ corresponding to the O–H, aromatic C–H and $C = C$ stretching frequencies. Comparison of the spectra indicate that the peak of O–H stretching is absent while the peak of $C = O$ stretching appeared in the product as a result of conversion of hydroquinone to quinone. To determine the stoichiometry, TBATB (0.482 g, 1.0 mmol) and hydroquinone (0.5505 g, 0.5 mmol) were mixed in 1:1 (V/V) acetic acid-water, this reaction mixture was allowed to stand for 24 hours, and the unreacted TBATB was determined spectrophotometrically at 394 nm. It was observed that the stoichiometry of the reaction is 1:1.

3 Results and Discussion

3.1 Effect of Reactants

The effects of oxidant, TBATB and reductant, hydroquinone were studied at 25 °C. The [hydroquinone] and [oxidant] concentrations were varied from 1.0×10^{-2} to $1.0 \times 10^{-1} \; mol \cdot dm^{-3}$ and 5×10^{-4} to $5 \times 10^{-3} \; mol \cdot dm^{-3}$, respectively. The values of rate constants remained constant (Table 1) as the concentration of oxidant is varied indicating first order dependence on the oxidant concentrations, while the values of rate constants were found to increase as the concentration of reductant increased. The Michaelis–Menten plot of $1/k_{obs}$ against 1/[hydroquinone] (Fig. 1) was found to be linear with the intercept indicating complex formation between the reactants prior to the rate determining step; therefore, the effect of [hydroquinone] was studied at different temperatures to evaluate the formation constant of the complex and the rate constant for its decomposition.

3.2 Effect of Solvent Composition

The effect of solvent composition on rate of the reaction was studied by varying the acetic acid content in the reaction mixture from 50 to 75% V/V. The pseudo-first order constant k_{obs} decreased (Table 2) as the acetic acid content increased.

Fig. 1 Michaelis–Menten plot of $1/k_{obs}$ against 1/[hydroquinone]; 10^3[TBATB] $= 1.0$ mol·dm^{-3}, 10^2[KBr] $= 1.0$ mol·dm^{-3}
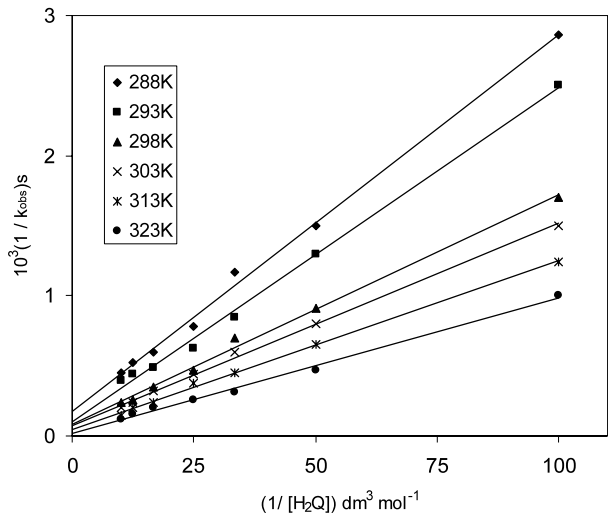
Table 2 Effect of acetic acid content on the k_{obs} values at 25 °C; 10^3[TBATB] $= 1.0$ mol·dm^{-3}, 10^2[H$_2$Q] $= 1.0$ mol·dm^{-3}, 10^2[KBr] $= 1.0$ mol·dm^{-3}

| % V/V Acetic acid	pH	$10^3 k_{obs}/\mathrm{s}^{-1}$
50	1.38	1.1
55	1.29	0.82
60	1.21	0.70
65	1.14	0.52
70	1.06	0.40
75	0.98	0.35

Table 3 Effect of temperature on the complex formation constant, K_c, rate constants, k_c, and activation parameters with respect to k_c

| Temp/K	288	293	298	303	313	323
$K_c/$ mol·dm^{-3}	3.4	4.3	4.9	5.3	6.1	9.1
$10^3 k_c/$ s^{-1}	5.8	9.8	12.3	13.0	20.0	49.8
$\Delta H^{\ddagger}/$ kJ·mol^{-1}			39.7 ± 0.4			
$\Delta S^{\ddagger}/$ J·K^{-1}·mol^{-1}			-145.3 ± 5			
$\Delta G^{\ddagger}/$ kJ·mol^{-1}			83.0 ± 0.4			

3.3 Effect of Temperature

The effect of [Hydroquinone] was studied at 15, 20, 25, 30, 40 and 50 °C and the formation constant of the complex between the reactants and the rate constant for its decomposition were determined from the linear $1/k_{obs}$ against 1/[hydroquinone] plots (Fig. 1). The activation parameters with respect to the rate determining decomposition of the complex were calculated and are given in Table 3.

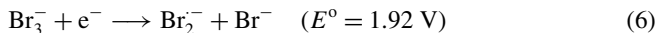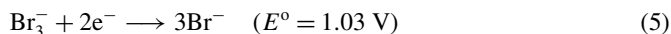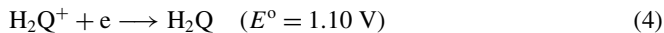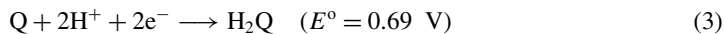**Fig. 2** Structure of the complex formed between H$_2$Q and Br$_3^-$
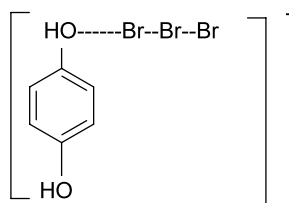
3.4 Mechanism and Rate Law

The reaction medium used in the present study is 50% V/V acetic acid in order to stabilize the oxidant in solution. The acetic acid content was further varied from 50 to 75% V/V in the reaction mixture. The pHs of different acetic acid solutions (Table 2) were measured and were found to vary from 1.38 to 0.98 for 50 and 75% V/V acetic acid solutions, respectively. The reported pK value of hydroquinone [8] is 9.85. Therefore, it exists in the protonated form in the pH range of the present study. The oxidant, TBATB, dissociates into a tetrabutylammonium ion and the tribromide ion in aqueous acetic acid [16] solutions and further decompositions of the tribromide ion also occur [17] as shown in equilibria given by Eqs. 1 and 2 respectively:

$$(C_4H_9)_4N^+Br_3^- \rightleftharpoons (C_4H_9)_4N^+ + Br_3^- \tag{1}$$

$$Br_3^- \rightleftharpoons Br_2 + Br^- \tag{2}$$
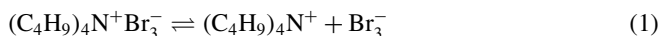
The second equilibrium can be shifted to left hand side by using an excess of bromide ion in the solutions. The active species of oxidant, TBATB, also does not undergo any protonation and in the presence of excess bromide ion in the present study; it exists as tribromide ion only. Thus the reactive species of the oxidant and the substrate are protonated hydroquinone, H$_2$Q, and tribromide ion, Br$_3^-$, respectively. The reaction was carried out under pseudo-first order conditions keeping the concentration of hydroquinone in large excess in 50% acetic acid solutions and also containing a constant quantity of 0.01 mol·dm^{-3} potassium bromide. The pseudo-first order plot was found to be linear for all kinetic runs and the rate constant, k_{obs}, values remained constant as the concentration of the oxidant was varied from 0.5×10^{-3} to 5.0×10^{-3} mol·dm^{-3} at constant concentration of hydroquinone of 0.01 mol·dm^{-3}, indicating an overall first order dependence of the reaction on the oxidant concentration. However, the pseudo-first order rate constants were found to increase with increases in the concentration of hydroquinone from 1.0×10^{-2} to 1.0×10^{-1} mol·dm^{-3} at constant TBATB concentration of 1.0×10^{-3} mol·dm^{-3}. The Michaelis–Menten plot of $1/k_{obs}$ against 1/[substrate] (Fig. 1) was found to be linear with intercept indicating that the mechanism involves a prior complex formation between the oxidant and the substrate followed by its rate determining decomposition. During the oxidation [17] of aliphatic alcohols by TBATB, prior complex formation between the non-bonded pairs of electrons of the alcohol oxygen and the tribromide ion has been predicted. Similarly, hydroquinone also contains an analogous phenolic OH group and the prior complex formation between the tribromide ion with the substrate occurs with the non-bonded pairs of electron of the phenolic oxygen (Fig. 2). The complex thus formed will decompose in the rate determining step. The oxidation of hydroquinone to quinone is a two-electron transfer process and in most of the reactions of hydroquinone the existence of the semiquinone radical has been predicted, irrespective of whether the oxidant is a two-electron or one-electron transfer reagent. The semiquinone radical thus produced preferentially undergos disproportionation generating
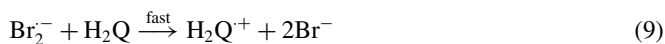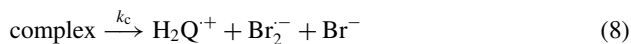
the final product, quinone. The E^o values for the oxidation of various protonated forms of hydroquinone and the semiquinone [8] radical are given Eqs. 3 and 4 respectively. From Eqs. 3 and 4 it can be noticed that the two-electron oxidation

$$Q + 2H^+ + 2e^- \longrightarrow H_2Q \quad (E^o = 0.69 \ \text{V}) \tag{3}$$

$$H_2Q^+ + e \longrightarrow H_2Q \quad (E^o = 1.10 \ \text{V}) \tag{4}$$

$$Br_3^- + 2e^- \longrightarrow 3Br^- \quad (E^o = 1.03 \ \text{V}) \tag{5}$$

$$Br_3^- + e^- \longrightarrow Br_2^{\cdot-} + Br^- \quad (E^o = 1.92 \ \text{V}) \tag{6}$$

of hydroquinone is thermodynamically more favorable than the one-electron oxidation. Even though the oxidant is capable of oxidizing hydroquinone through a direct two-electron transfer process, single electron transfer mechanisms have been proposed. Recently, the mechanism of oxidation of hydroquinone was studied using trans-dioxoruthenium(VI) [8] and μ-oxo-bridged di-iron(III, III) [12] complexes. In the reaction utilizing the ruthenium(VI), complex, it has been shown that the one electron-transfer mechanism is favored thermodynamically even though the E^o value of the two-electron change from Ru(VI) to Ru(IV) (0.96 V) is higher than that of the Ru(VI)/Ru(V) (0.56 V) redox couple. Similarly μ-oxo-bridged-di-iron(III, III) follows a one-electron reduction producing the semiquinone radical. In the present study also the oxidant Br_3^- is a two-electron oxidant having an E^o value of 1.03 V [20] with bromide ion as the product, whereas the E^o value is 1.92 V [21] for the $Br_2^{\cdot-}$ to $2Br^-$ one electron change. The redox reactions of tribromide ion and protonated hydroquinone with the corresponding E^o values are summarized in Eqs. 3 to 6. Combination of two electron-transfer and one electron-transfer reactions of the oxidant and the reductant couples leads to ΔG^o values of 65.62 kJ·mol^{-1} and 79.13 kJ·mol^{-1} respectively. The requirement of facile electron transfer is that $\Delta G^o < \Delta G^*$ and both calculated values of ΔG° are less than the ΔG^* value obtained in the present study for the slow step of the reaction. Therefore, in order to differentiate between the two possibilities, the second-order rate constants have been calculated using $k = 10^{13} \times e^{-\Delta G^o/RT}$ [9]. The calculated rate constant for two-electron transfer at 298 K was 31.6 dm^3·mol^{-1}·s^{-1} and for a one-electron path it was 0.134 dm^3·mol^{-1}·s^{-1}. The experimentally obtained pseudo-first-order rate constant is 1.1×10^{-3} s^{-1} (Table 1) and for the concentration of hydroquinone of 1.0×10^{-2} mol·dm^{-3} the second order rate constant was found to be 0.1 dm^3·mol^{-1}·s^{-1}, which is of the same order as the calculated value considering the one-electron path. Thus the oxidation of hydroquinone follows the one-electron transfer mechanism rather than the two electron-transfer mechanism which is also predicted in the oxidation of hydroquinone by both Ru(VI) and μ-dioxo-bridged-di-iron(III,III) ions. The driving force for the one-electron transfer in oxidation of hydroquinone might be due to the fast disproportionation of the resulting semiquinone radical. The activation energy for semiquinone disproportionation is reported to be 15.5 kJ·mol^{-1} which is close to the diffusion controlled limit (12.5 kJ·mol^{-1}) [22]. Thus the combination of semiquinone radical as a result of a one-electron transfer step is facilitated over that of the direct two-electron step. Therefore, the oxidation of hydroquinone by TBATB involves a one electron-transfer process producing both H_2Q^+ and $Br_2^{\cdot-}$ radicals. The bromine radical reacts with another hydroquinone molecule in a fast step to generate the protonated semiquinone radical. The semiquinone radical undergoes rapid disproportionation ($k = 1.1 \times 10^9$ mol^{-1}·dm^3·s^{-1}) [8] to yield the product quinone.

Scheme 1

$$Br_3^- + H_2Q \underset{\rightleftharpoons}{\overset{K_c}{}} \text{complex} \tag{7}$$

$$\text{complex} \xrightarrow{k_c} H_2Q^{\cdot+} + Br_2^{\cdot-} + Br^- \qquad (8)$$

$$Br_2^{\cdot-} + H_2Q \xrightarrow{\text{fast}} H_2Q^{\cdot+} + 2Br^- \qquad (9)$$

$$2H_2Q^{\cdot+} \xrightarrow{\text{fast}} H_2Q + Q + 2H^+ \qquad (10)$$

The overall mechanism of the reaction can be summarized as in Scheme 1. According to Scheme 1 the active species of the oxidant and the hydroquinone are respectively Br_3^- and protonated hydroquinone. These two active species will form a complex as shown by Eq. 7 of Scheme 1. The complex formed undergoes slow decomposition to generate the semiquinone free radical and bromine free radical as a result of one-electron transfer between them as shown by Eq. 8. In step 9 the bromine free radical produced rapidly oxidizes another hydroquinone, and in step 10 the fast disproportionation of the semiquinone occurs. The rate of the reaction is given by Eq. 11:

$$\text{Rate} = k_c[\text{complex}] \qquad (11)$$

The concentration of the complex can be obtained from step (7) of Scheme 1 as in Eq. 12 where $[H_2Q]_{\text{free}}$ is the concentration of free hydroquinone. The $[H_2Q]_{\text{free}}$ can be expressed as in Eq. 13 in terms of total concentration of hydroquinone.

$$[\text{complex}] = K_c[Br_3^-][H_2Q]_{\text{free}} \qquad (12)$$

$$[H_2Q]_{\text{free}} = \frac{[H_2Q]}{1 + K_c[H_2Q]} \qquad (13)$$

Substituting the value of $[H_2Q]_{\text{Free}}$ in Eq. 12 and the resulting equation in Eq. 11

$$\text{Rate} = \frac{k_c K_c[Br_3^-][H_2Q]}{1 + K_c[H_2Q]} \qquad (14)$$

$$k_{\text{obs}} = \frac{k_c K_c[H_2Q]}{1 + K_c[H_2Q]} \qquad (15)$$

we get the rate law, Eq. 14.

The corresponding expression for the pseudo-first-order rate constant is given by Eq. 15. Verification of Eq. 15 can be done by plotting $1/k_{\text{obs}}$ against $1/[H_2Q]$, which was found to be linear. Such Michaelis–Menten plots were obtained at five different temperatures (Fig. 1) and from the values of the intercept and slope of the linear plots the complex formation constant, K_c, and the rate constant for the slow step of the reaction, k_c, were determined (Table 3). Further, using the values of the k_c at different temperatures, the activation parameters for the slow step of the reaction were calculated and the values are given in Table 3.

The increase in the acetic acid content in the reaction medium changes both the pH as well as the dielectric constant of the medium. The highest pH value of 1.38 is obtained in solutions containing 50% V/V acetic acid. At this pH the hydroquinone will be present in the protonated form as its pK value is low [8]. Therefore, the effect of acetic acid content on the rate of the reaction will be only due to the change in the dielectric constant of the medium. The increase in the acetic acid content was found to decrease the rate of reaction and the plot of $\log_{10} k_{\text{obs}}$ against $1/D$, where D is dielectric constant of the medium, was non-linear. Therefore the solvent effect was analyzed according to the Grunwald-Winstein [23] equation (Eq. 16), where Y is the solvent parameter representing the ionizing power of the solvent

and m is the measure of the extent of ion-pair formation in the transition state. The value of m is also taken as the ratio of $[(S_N1/S_N2) = 0.5]$ pathways involved in the transition state, and a value less than 0.5 indicates an S_N2 pathway while a value greater than 0.5 indicates an S_N1 pathway. In the present study the plot of $\log_{10} k_{obs}$ against Y [22] was found to be linear ($R = 0.998$) with a slope of 0.43

$$\log_{10} k = \log_{10} k_o + mY \tag{16}$$

which is less than 0.5 indicating an reaction follows an S_N2 mechanism. Therefore, the formation of the complex between hydroquinone and TBATB occurs through the interaction between the non-bonded pairs of electrons of the phenolic OH and the tribromide ion as shown in Fig. 2. The dissociation of the phenolic OH or the proton transfer before formation of the complex would have resulted in a slope of more than 0.5 for the Grunwald-Winstein plot and the mechanism would have followed an S_N1 mechanism. Since, the dissociation of hydroquinone to HQ^+ is not possible under the reaction conditions and the slope of Grunwald-Winstein plot also supports the formation of the complex as shown in Fig. 2. The decrease in entropy of the reaction is also in support for the formation of a complex analogous to that in the case of oxidation of aliphatic alcohols by TBATB [17].

4 Conclusions

The reaction between hydroquinone and tetrabutylammonium tribromide in 50% aqueous acetic acid solution proceeds with formation of an S_N2 type complex between the reactants followed by its slow decomposition. The complex formation is supported by the Michaelis–Menten plots. The active species of the oxidant and substrate were found to be tribromide ion and hydroquinone respectively. The mechanism involving a single-electron transfer is favored due to the facilitated disproportionation of the semiquinone radical generated rather than that of two electron-transfers. The semiquinone radical disproportionates rapidly to form the product quinone. The S_N2 type mechanism was supported by the Grunwald-Winstein plot with a slope less than 0.5 for the effect of solvent on the reaction.

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